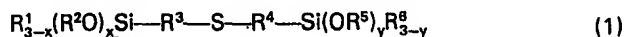


# (12) UK Patent Application (19) GB (11) 2 028 850 A

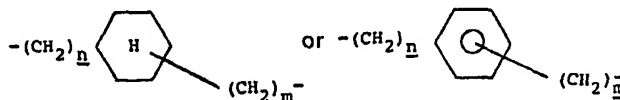
- (21) Application No 7927707  
 (22) Date of filing 8 Aug 1979  
 (23) Claims filed 8 Aug 1979  
 (30) Priority data  
 (31) 2834691  
 (32) 8 Aug 1978  
 (33) Fed. Rep. of Germany (DE)  
 (43) Application published  
 12 Mar 1980  
 (51) INT CL<sup>3</sup>  
 C07F 7/18 C08G 77/22  
 C09C 3/12  
 (52) Domestic classification  
 C3S 1C 3A 5 7B 7D 8 9  
 C1A 13 310 312 519 N34  
 VF1  
 C2C 20Y 21X 228 248  
 30Y 350 360 361 366 367  
 368 36Y 37X 408 43X  
 569 623 628 66Y CE CQ  
 FB TH YK  
 C3T 1 2 7B2 7C 7E1 7J2  
 8A  
 C3Y B230 F101  
 (56) Documents cited  
 GB 1527598  
 GB 1448826  
 GB 791609  
 DE 2550660A  
 (58) Field of search  
 C3S  
 C3T  
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## (54) Complex rhodium compounds

(57) Complex compounds of rhodium contain at least one sulphide corresponding to the general formula



co-ordinatively bound to the central atom, its still free co-ordination sites, if any, being occupied by carbon monoxide, an olefin, amine, phosphine or nitrile and any charge satisfied by a chloride, bromide, iodide, acetate, trifluoroacetate, propionate or hydride ion; R<sup>1</sup> and R<sup>6</sup> representing a C<sub>1-6</sub> alkyl group, a C<sub>6-8</sub> cycloalkyl radical, an optionally substituted benzyl or phenyl radical or chloride or bromide, R<sup>2</sup> and R<sup>5</sup> representing a C<sub>1-6</sub> alkyl group, a C<sub>6-8</sub> cycloalkyl group, an optionally substituted phenyl or benzyl group or a 2-methoxyethyl or 2-ethoxyethyl group, R<sup>3</sup> and R<sup>4</sup> representing a C<sub>1-10</sub> alkylene group, a phenylene or C<sub>5-8</sub> cycloalkylene group optionally substituted by a methyl, ethyl, propyl or iso-propyl group, or a group



where *n* and *m* are 0 to 5 and the ring H-atoms may be partly replaced by halogen or cyanide, and *x* and *y* are 1, 2 or 3 or may be 0 when R<sup>1</sup> or R<sup>6</sup> represents chlorine or bromine.

These complexes, or polysiloxanes containing units derived therefrom, or inorganic supports treated therewith, are useful as catalysts for chemical reactions.

Certain of the chemical formulae appearing in the printed specification were submitted in formal form after the date of filing.

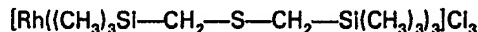
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## SPECIFICATION

**Monomeric, polymeric and support-fixed complex rhodium compounds, a process for their production and their use as catalysts**

This invention relates to co-ordination compounds of rhodium with silicon-substituted dialkyl or diaryl sulphide groups as ligands in monomeric, polymeric and support-fixed form, to a process for their production and to their use as catalysts. 5

Rhodium compounds containing sulphide groups have been known for some time (J. C. S. Dalton 1973, 116; J. Prakt. Chem. 375, 106, 1973). German Offenlegungsschrift No. 2,405,274 describes rhodium complexes of trivalent rhodium with ligands (SR'R'') which correspond for example to the following formula 10

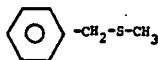


They are intended to be used as homogenous catalysts for hydrosilylation reactions. In this case, the divalent sulphur of the ligand is symmetrically attached to a trimethyl silyl group through a methylene group. Accordingly, the valencies of the two silicon atoms are saturated with non-functional, that is to say inert, i.e. for example hydrolysis-stable groups. Accordingly, compounds such as these can only be used as catalysts in the homogeneous phase. 15

German Offenlegungsschrift No. 2,453,299 also describes complex compounds of trivalent rhodium which, in accordance with the formula



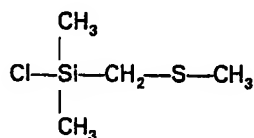
contains sulphide ligands having for example the following composition: 20



These compounds are intended to be used for hydroformylation reactions. They are also used in the homogeneous phase.

One disadvantage of using these known substances for catalytic purposes lies in the fact that their separation from constituents of the reaction mixture and, hence, their recovery is both difficult and expensive. In addition, the losses of expensive noble metal which are incurred represent a not significant cost factor in the large-scale working of corresponding catalysis processes. 25

Finally, German Offenlegungsschrift No. 2,550,660 describes inorganic catalyst supports, such as SiO<sub>2</sub>, surface-modified by sulphur-containing organosubstituted silyl groups which are co-ordinately attached through the sulphur atoms to form a complex of platinum or rhodium. For their production, a compound of the following type for example 30



is reacted with the surface silanol groups of the support material to form a structure of the following formula:

support—O—Si(CH<sub>3</sub>)<sub>2</sub>—CH<sub>2</sub>—S—CH<sub>3</sub> 35

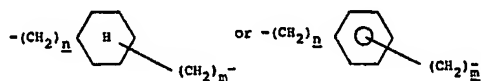
The support modified in this way is then reacted with a compound of platinum or rhodium. In one variant, the sulphur-containing silane may even be initially reacted with a platinum or rhodium compound and the complex obtained subsequently reacted with the support. The catalyst-modified supports are intended to be used for hydro-formylation, oligomerisation or hydrosilylation reactions. Their main feature lies in the fact that the ligand carrying the catalytically active metal is only attached to the support through a single silicon atom via oxygen bridges. The residues on the sulphur which are not bound to the support do not make any contribution towards fixing. 40

The present invention provides new heterogenisable complex compounds of rhodium in which at least one sulphide corresponding to the general formula

$\text{R}_3^{1-x}(\text{R}^2\text{O})_x\text{Si}-\text{R}^3-\text{S}-\text{R}^4-\text{Si}(\text{OR}^5)_y\text{R}_3^{6-y}$  (1) 45

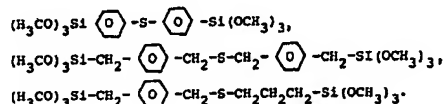
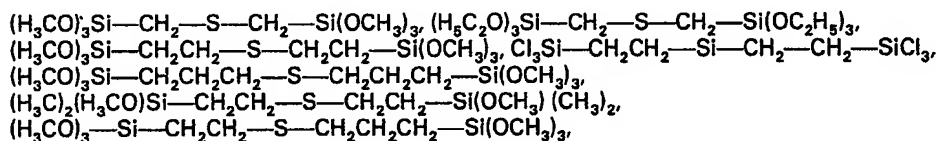
is co-ordinately bound to the central atom, its still free co-ordination sites, if any, being occupied by

carbon monoxide, an olefin, amine, phosphine or nitrile and a necessary charge exchange with a chloride, bromide or iodide ion, an acetate, trifluoroacetate or propionate ion having been completed, optionally with complete or partial replacement or these anions by a hydride ion; in formula (1), R<sup>1</sup> and R<sup>6</sup> representing a straight-chain or branched alkyl group containing from 1 to 5 carbon atoms, a cycloalkyl radical containing from 5 to 8 carbon atoms, a benzyl or phenyl radical optionally substituted by one or more methyl, ethyl, propyl, methoxy, ethoxy groups, NO<sub>2</sub>-groups, halide or cyanide and also chloride or bromide; R<sup>2</sup> and R<sup>5</sup> representing a straight-chain or branched alkyl group containing from 1 to 5 carbon atoms, a cycloalkyl group containing from 5 to 8 carbon atoms, an optionally substituted phenyl or benzyl group or a 2-methoxyethyl or 2-ethoxyethyl group, R<sup>2</sup> and R<sup>5</sup> being the same or different; R<sup>3</sup> and R<sup>4</sup> representing a straight-chain or branched alkylene group containing from 1 to 10 carbon atoms, a phenylene or cycloalkylene group containing from 5 to 8 carbon atoms optionally substituted by a methyl, ethyl, propyl or iso-propyl group and units of the type



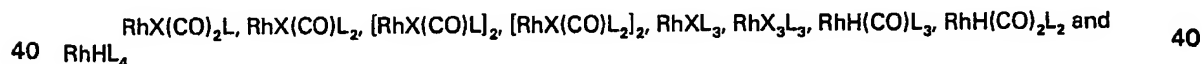
- 15 where  $n$  and  $m$  may be a number from 0 to 5 and the ring H-atoms may be partly replaced by halogen, particularly F, Cl, Br, or a cyanide group, R<sup>3</sup> and R<sup>4</sup> being the same or different, and  $x$  and  $y$  may be the number 1, 2 or 3 or may be 0 when R<sup>1</sup> or R<sup>6</sup> represents chlorine or bromine,  $x$  and  $y$  being the same or different.

- 20 The silicon-containing sulphides corresponding to formula (1) are compounds known *per se* and may be obtained by known processes, as described for example in German Auslegeschrift No. 1,000,817. The following are examples of these compounds:



- 30 One advantage of the rhodium complexes according to the invention with ligands corresponding to formula (1) over the known sulphur-containing rhodium compounds discussed at the beginning lies in particular in the fact that they may readily be converted into a form which is insoluble in organic media and, where they are used as catalysts, thus enable liquid constituents of the reaction mixture to be conveniently separated by filtration, centrifuging or decantation. By virtue of this so-called "heterogenisation", the rhodium losses can be reduced to a minimum. They allow heterogenisation by chemical fixing to the surface of certain support materials, the two silicon atoms being bound to the support through oxygen bridges. However, they may also be reacted to form polymeric solids where they are provided with trifunctional groups on the silicon.

The stoichiometric composition of the new rhodium compounds may be represented by the following formulae:



in which the rhodium is present in the valency states 0, +1 or +3, L is a ligand corresponding to formula (1) and X represents chlorine, bromine, iodine, acetate, trifluoroacetate or propionate.

Particularly preferred complex compounds have the following stoichiometric composition:



- 45 In which sulphide compounds corresponding to formula (1) are present as ligands L and X represents chlorine, bromine, iodine, acetate, trifluoroacetate or propionate. Where they are used as catalysts, they may be activated or influenced in regard to their selectivity by after-treatment with H<sub>2</sub> and CO in a solvent, such as benzene, toluene, xylene, *n*-hexane, cyclohexane, methyl cyclohexane, monoglyme, diethyl ether, tetrahydrofuran, dioxane and, in particular, lower alcohols, under total pressures of from 10 to 300 bars and at temperatures of from 50 to 200°C.

Other preferred complex compounds have the following stoichiometric composition:

$$\text{RhCl}(\text{CO})\text{L}_2$$

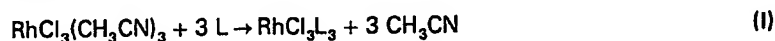
in which sulphide compounds corresponding to formula (1) are present as ligands L.

During their use as catalysts, changes may occur both in the valency state of the rhodium and in the number and type of bound ligands. In addition, X in the formula  $\text{RhX}_3\text{L}_3$  may be partly replaced by hydrogen whilst the sulphide ligands L in the formulae  $\text{RhX}_3\text{L}_3$  and  $\text{RhCl}(\text{CO})\text{L}_2$  may be partly replaced by other donors, such as carbon monoxide, olefins, amines, phosphines or nitriles.

The preferred rhodium complex  $\text{RhX}_3\text{L}_3$  is obtained by reacting sulphides corresponding to general formula (1) with rhodium compounds representing anhydrous salts of a hydrohalic acid or a lower organic carboxylic acid and optionally containing readily displaceable ligands, preferably lower aliphatic nitriles or benzonitrile. Their catalytic activity may be influenced by aftertreatment with hydrogen and carbon monoxide in a solvent, such as benzene, toluene, xylene, *n*-hexane, cyclohexane, methyl cyclohexane, monoglyme, diethyl ether, tetrahydrofuran, dioxane and, in particular, lower alcohols, under total pressures of from about 10 to 300 bars and at temperatures of from 50 to 200°C.

Accordingly, the complexes  $\text{RhX}_3\text{L}_3$  may readily be produced by reacting the sulphides corresponding to formula (1) with known, readily obtainable compounds such as, for example  $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ ,  $\text{RhBr}_3 \cdot 2\text{H}_2\text{O}$ ,  $\text{RhI}_3$ ,  $\text{RhCl}_3(\text{CH}_3\text{CN})_3$ ,  $\text{RhCl}_3(\text{C}_2\text{H}_5\text{CN})_3$ ,  $\text{RhCl}_3(\text{C}_6\text{H}_5\text{CN})_3$ ,  $\text{RhBr}_3(\text{CH}_3\text{CN})_3$  or other rhodium systems containing readily substitutable ligands. In practice, it is preferred to use  $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$  and  $\text{RhCl}_3(\text{CH}_3\text{CN})_3$ , of which the production is described by B. F. G. Johnson and R. A. Walton in J. Inorg. Nucl. Chem. 28, 1901 (1966).

For producing pure complexes according to the invention having the composition  $\text{RhX}_3\text{L}_3$ , it is necessary on account of the hydrolysis-sensitive groups on the silicon to use an anhydrous rhodium starting compound such as, for example,  $\text{RhI}_3$  or  $\text{RhCl}_3(\text{CH}_3\text{CN})_3$ , in which case the reaction takes place in accordance with the following equation:

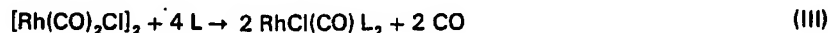


The reaction may be carried out in pure substance, although it is preferably carried out in apolar or polar inert and anhydrous solvent and takes place at temperatures as low as room temperature. In order to accelerate the reaction, it may be of advantage to apply temperatures between 20°C and the reflux temperature of the solvent used. In order not unnecessarily to complicate the purification of the compounds obtained, the sulphide ligands L corresponding to formula (1) are preferably used in substantially stoichiometric quantities. By a halogen exchange on the central atom, it is also possible to synthesise the bromides and iodides  $\text{RhBr}_3\text{L}_3$  and  $\text{RhI}_3\text{L}_3$  in accordance with the following equation:



The complex compounds corresponding to the formula  $\text{RhCl}(\text{CO})\text{L}_2$  may be produced by reacting sulphides corresponding to general formula (1) with  $[\text{Rh}(\text{CO})_2\text{Cl}]_2$  at a temperature below 100°C, the reaction being carried out in an apolar or polar inert and anhydrous solvent, such as benzene, toluene, *n*-hexane, *n*-pentane, cyclohexane methyl, cyclohexane, petroleum ether, methanol, ethanol, propanol, isopropanol, diethyl ether, tetrahydrofuran, monoethylene glycol dimethyl ether, acetone, at temperatures between room temperature and the boiling temperature of the solvent.

Accordingly, the starting material used in this case is  $[\text{Rh}(\text{CO})_2\text{Cl}]_2$  of which the production is described in Inorg. Synth. 8, 211 (1966). The reaction takes place in accordance with equation (III) below and, providing the necessary stoichiometry is maintained, the intermediate stage initially formed, which has the composition  $\text{RhCl}(\text{CO})_2\text{L}$ , can be isolated:



The reaction according to equation (III) may be carried out both at room temperature and also at higher temperatures. Although higher temperatures have a favourable effect on the reaction time, they can also give rise to decomposition of the product if they exceed approximately 100°C. The solvents used for this synthesis may be either polar or apolar in character. However, they should not enter into any competitive or secondary reactions with the groups on the silicon and must be substantially anhydrous for the discussed case where the complex compounds according to the invention are produced in pure form. This generally applies to the reactions according to equations (I) to (III).

As already mentioned, an advantage of the complex compounds according to the invention, particularly those corresponding to the formula  $\text{RhX}_3\text{L}_3$ , lies in the fact that they may readily be heterogenised, i.e. converted into a substantially insoluble form which enables them to be used in known manner for heterogeneous catalysis with their catalytic properties intact. This may be done by completely or partly splitting off the groups  $\text{R}^1$ ,  $\text{OR}^2$  and  $\text{OR}^3$ ,  $\text{R}^4$  present on the ligand L by hydrolysis in the form of alcohols or phenols or in the form of HCl or HBr and providing the remaining silicon atoms containing alkylene sulphide or arylene sulphide groups with a polymeric structure. The number of

functional groups attached to the silicon will determine whether a more syrupy mass or a silica-like structure is formed.

- An important subject of the invention are polymeric compounds having a silica-like structure and the function of a rhodium support which are sparingly soluble in organic solvents and to which rhodium salts of a hydrohalic acid or a lower organic carboxylic acid optionally containing carbon monoxide, olefin, amine, phosphine or nitrile ligands are co-ordinatively bound through at least one ligand L', L' representing a sulphide compound L with trifunctionally substituted silicon corresponding to formula (1), in which the groups OR<sup>2</sup> and OR<sup>6</sup>, R<sup>1</sup> and R<sup>8</sup> originally present — the latter preferably in the form of chlorine or bromine ions — are partly or completely split off hydrolytically as alcohol or phenol, HCl or HBr and in which a ratio of rhodium to sulphide of from 1:1 to 1:10<sup>6</sup> is present, obtained by reacting complex compounds having the stoichiometric composition RhX<sub>3</sub>L<sub>3</sub>, in which L represents at least one ligand corresponding to formula (1) and carbon monoxide, olefin, amine, phosphine or nitrile bound to still free co-ordination sites, if any, and X represents chlorine, bromine, iodine, acetate, trifluoroacetate or propionate with water or an aqueous acid solution, optionally in the presence of an excess of the sulphide L over and above the stoichiometric composition RhX<sub>3</sub>L<sub>3</sub> and/or in the presence of crosslinking agents, such as methyl or ethyl silicate, optionally with removal of alcohol or phenol formed by distillation, or by reacting the ligand L with water or an aqueous acid solution, optionally in the presence of crosslinking agents of the above-mentioned type and optionally with removal of alcohol or phenol formed by distillation, and reacting the solid formed with rhodium compounds representing aqueous or anhydrous salts of a hydrohalic acid or a lower carboxylic acid and optionally containing readily displaceable ligands, preferably lower aliphatic nitriles or benzonitrile, or with the compound [Rh(CO)<sub>2</sub>Cl]<sub>2</sub>.

- The present invention also providing a process by which the polymers characterised above can be produced. In this process complex compounds having the stoichiometric composition RhX<sub>3</sub>L<sub>3</sub>, in which L represents at least one ligand of formula (1) provided with trifunctionally substituted silicon and carbon monoxide, olefin, amine, phosphine or nitrile bound to still free co-ordination sites, if any, and X represents chlorine, bromine, iodine, acetate, trifluoroacetate or propionate are reacted with water or an aqueous acid solution, optionally in the presence of an excess of the sulphide L over and above the stoichiometric composition RhX<sub>3</sub>L<sub>3</sub> and/or in the presence of crosslinking agents, such as methyl or ethyl silicate, optionally with simultaneous or subsequent removal of alcohol or phenol formed by distillation, or the ligand L is reacted with water or an aqueous acid solution, optionally in the presence of crosslinking agents of the above-mentioned type and optionally with simultaneous or subsequent removal of alcohol or phenol formed by distillation, and the solid formed is reacted with rhodium compounds representing aqueous or anhydrous salts of a hydrohalic acid or a lower carboxylic acid and optionally containing readily displaceable ligands, preferably lower aliphatic nitriles or benzonitriles, or with the compound [Rh(CO)<sub>2</sub>Cl]<sub>2</sub>.

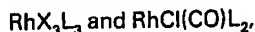
- Accordingly, to convert a complex of the RhX<sub>3</sub>L<sub>3</sub>-type with ligands L corresponding to formula (1) — preferably RhCl<sub>3</sub>L<sub>3</sub> with preferably trifunctionally substituted silicon — into its substantially insoluble form, it is best to treat the rhodium complex present in pure substance or even dissolved in an organic solvent with an excess of water either at room temperature or at elevated temperature and, in order to obtain substantially quantitative elimination, simultaneously or subsequently to remove the alcohol or phenol formed from the reaction mixture by distillation. Heterogenisation is particularly simple in the case of ligands which have chlorine or bromine atoms on the silicon and which build up a silica-like structure with elimination of HCl or HBr. By adopting this method, it is possible in particular to introduce even more ligands L into the precipitated product than are necessary according to the stoichiometry of the formula RhX<sub>3</sub>L<sub>3</sub>, in which case it is best to hydrolyse a mixture consisting of the required quantity of ligands L, the RhX<sub>3</sub>L<sub>3</sub> complex and, optionally, a solvent. In this way, it is possible if necessary to influence the service life, the selectivity and the activity of the catalyst. In addition, the separation of the rhodium from the ligand-containing solid is made very difficult. By the presence of so-called crosslinkers, which also represent readily hydrolysable compounds, such as for example Si(OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub>, it is also possible to facilitate precipitation and to vary the density of sulphide groups in the precipitated product. In order to incorporate large excesses of free ligand L into the precipitated product, it is best to use for hydrolysis a dilute aqueous acid solution, preferably dilute hydrochloric acid, into which the dissolved or undissolved mixture of the particular ligand L and RhX<sub>3</sub>L<sub>3</sub>-complex, preferably RhCl<sub>3</sub>L<sub>3</sub> is introduced dropwise, or vice versa.

- In practice, a catalyst "heterogenised" in this way, in which the polymeric ligands simultaneously perform the function of a support and which may have an atomic ratio of Rh to S of from 1:1 to 1:10<sup>6</sup>, is not produced from the pure RhX<sub>3</sub>L<sub>3</sub> compounds, but instead from a rhodium compound from the series RhCl<sub>3</sub>·3H<sub>2</sub>O, RhBr<sub>3</sub>·2H<sub>2</sub>O, RhI<sub>3</sub>, RhCl<sub>3</sub>(CH<sub>3</sub>CN)<sub>3</sub>, RhCl<sub>3</sub>(C<sub>2</sub>H<sub>5</sub>CN)<sub>3</sub>, RhCl<sub>3</sub>(C<sub>6</sub>H<sub>5</sub>CN)<sub>3</sub>, RhBr<sub>3</sub>(CH<sub>3</sub>CN)<sub>3</sub> or other rhodium systems containing readily substitutable ligands, which is reacted with the required quantity of sulphide compound L either in pure substance or in solution to form the complex compound RhX<sub>3</sub>L<sub>3</sub> which, optionally after the solvent has been changed to avoid a back reaction, i.e. for example after ethanol has been replaced by toluene, is hydrolysed by precipitation with water or an aqueous acid solution, optionally with removal of the alcohol or phenol formed by distillation.

- An alternative to this is to use a support to which the rhodium complexes may be attached through the

silicon groups in the sulphide ligand. Suitable support materials are, above all, inorganic substances which contain reactive surface groups, particularly acid OH-groups, which can react with the  $\text{SiOR}^2$ ,  $\text{SiOR}^5$  or  $\text{SiR}^1$ ,  $\text{SiR}^6$  units corresponding to formula (1) with elimination of alcohol or phenol or with elimination of HCl or HBr to form support  $\text{—O—Si—}$  bonds and, through the double linkage sites per ligand, guarantee particularly firm linkage between the rhodium complex and the support material.

Accordingly, the present invention also provides complex rhodium compounds bound through inorganic supports containing surface oxygen atoms, of the type



in which X represents chlorine, bromine, iodine, acetate, trifluoroacetate or propionate and L represents at least one ligand corresponding to formula (1) and carbon monoxide, olefin, amine, phosphine or nitrile bound to still free co-ordination sites, if any, through which the bond with the support is established by reaction of the acid hydrogen with the groups  $\text{OR}^2$  and  $\text{OR}^5$ ,  $\text{R}^1$  and  $\text{R}^6$  originally present — the latter preferably in the form of chlorine or bromine ions, with elimination of alcohol or phenol, HCl or HBr, any still unco-ordinated residues of the sulphide L being bound to the support and rhodium:sulphide ratios of from 1:1 to 1:10<sup>3</sup> being present, obtained by treating a solution of the compound  $\text{RhX}_3\text{L}_3$  or  $\text{RhCl}(\text{CO})\text{L}_2$  with a suspension of the support material in an inert organic solvent, optionally in the presence of excess sulphides L of formula (1) within the quantitative ratio limits specified, at temperatures between room temperature and the reflux temperature of the suspending agent used, or by treating a sulphide of formula (1) with a suspension of the support material in an inert organic solvent under the temperature conditions specified and subsequently reacting the solid form with rhodium compounds representing anhydrous or aqueous salts of a hydrohalic acid or a lower carboxylic acid and optionally containing readily displaceable ligands, preferably lower aliphatic nitriles or benzonitrile, or with the compound  $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ .

Although there is no limit to the choice of support materials which may be used, the following support materials have proved to be particularly suitable: pyrogenic or precipitated silica, quartz, a silicate-containing glass, silica gel, titanium dioxide, zirconium dioxide, a zeolite, aluminium oxide, kaolin, bauxite, diatomaceous earth or any other substance containing acid OH-groups synthesised from oxide compounds of aluminium and silicon and salts or oxides of other metals.

To produce the support-fixed complex rhodium compounds, it has proved to be of advantage to use a process in which a solution of the compound  $\text{RhX}_3\text{L}_3$  or  $\text{RhCl}(\text{CO})\text{L}_2$  is treated with a suspension of the support material in an inert organic solvent, optionally in the presence of excess sulphides L corresponding to formula (1) at temperatures between room temperature and the reflux temperature of the suspending agent used, or a sulphide corresponding to formula (1) is treated with a suspension of the support materials in an inert organic solvent under the specified temperature conditions, after which the solid formed is reacted with rhodium compounds representing anhydrous or aqueous salts of a hydrohalic acid or a lower carboxylic acid and optionally containing readily displaceable ligands, preferably lower aliphatic nitriles or benzonitrile, or with the compound  $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ .

In one embodiment of the process according to the invention which is preferred for practical application, a rhodium compound from the series  $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ ,  $\text{RhBr}_3 \cdot 2\text{H}_2\text{O}$ ,  $\text{RhI}_3$ ,  $\text{RhCl}_3(\text{CH}_3\text{CN})_3$ ,  $\text{RhCl}_3(\text{C}_2\text{H}_5\text{CN})_3$ ,  $\text{RhCl}_3(\text{C}_6\text{H}_5\text{CN})_3$ ,  $\text{RhBr}_3(\text{CH}_3\text{CN})_3$  and  $[\text{Rh}(\text{CO})_2\text{Cl}]_2$  or other rhodium systems containing readily substitutable ligands, is reacted with the required quantity of sulphide compound L in pure substance or in solution to form the complex compound  $\text{RhX}_3\text{L}_3$  or  $\text{RhCl}(\text{CO})\text{L}_2$  which is then treated with a suspension of the support material, optionally after the solvent has been changed to avoid a back reaction, i.e. after ethanol has been replaced by toluene for example.

In order to avoid hydrolysis of the moisture-sensitive functional groups on the silicon, it is of course best to react a substantially anhydrous starting complex, such as for example  $\text{RhCl}_3(\text{CH}_3\text{CN})_3$ , with the calculated quantity of sulphide compounds, the atomic ratio of rhodium to sulphur amounting to between 1:1 and 1:10<sup>3</sup>. This is followed by direct further reaction with a suspension of the support material, best at elevated temperatures. It is also possible to adopt the reverse procedure—primary fixing of the ligand L to the support, followed by reaction with  $\text{RhCl}_3(\text{CH}_3\text{CN})_3$  for example. Suitable solvents both for producing and for fixing the complex containing sulphide groups are, for example, benzene, toluene, xylene, cyclohexane, or *n*-hexane. For producing and fixing the rhodium-sulphide complex, it is preferred to apply relatively high temperature, although both stages may also be carried out at room temperature.

The rhodium-containing solids produced with or without a support, i.e. the polymerised and the support-fixed complex compounds, may be optimised in regard to activity and selectivity where they are to be used as catalysts. To this end, the polymeric solid or the support-fixed complex rhodium compounds may be aftertreated in one or more stages with hydrogen/carbon monoxide mixtures and/or with reducing agents, such as formaldehyde, alkali or alkaline-earth borohydride, borane compounds, lithium aluminium hydrides or hydrazine, under total pressures of from about 10 to 300 bars and at temperatures of from 50 to 200°C, preferably in the presence of a solvent, such as benzene, toluene, xylene, *n*-hexane, cyclohexane, methyl cyclohexane, monoglyme, diethyl ether, tetrahydrofuran, dioxane and, in particular, lower alcohols. It is also possible if necessary to carry out a reduction treatment in

pure substance.

The soluble, precipitated and support-fixed rhodium complexes according to the invention, above all their reduced forms, are excellent catalysts for hydroformylation, hydrogenation, oligomerisation, carbonylation, carboxymethylation and isomerisation reactions and for reactions of CO with H<sub>2</sub>. After they have been used in homogeneous systems for catalytic processes, the soluble catalysts may even be heterogenised by polymerisation or fixing to supports and separated in this form from the reaction mixture. Where the object of heterogenisation is to obtain a syrupy mass rather than a solid, it is best to start with monomeric complex compounds in which the silicon is difunctionally substituted. Where heterogenisation is carried out by fixing to a support, the functionality of the groups on the silicon is of minor importance.

Finally, the present invention provides the use of the monomeric, polymeric and support-fixed complex rhodium compounds as catalysts for chemical reactions.

Thus, the hydroformylation of olefins using the new catalysts may be carried out in known manner under total hydrogen/carbon monoxide pressures of from 10 to 1000 bars and at temperatures of from about 70 to 200°C in the presence or absence of a solvent, the high selectivity of the new catalysts enabling aldehydes or the corresponding alcohols to be subsequently produced.

The hydrogenation of olefinic groups may be carried out at room temperature or elevated temperatures, under pressures below or above atmospheric pressure and, of course, at atmospheric pressure. In this case, the "heterogenised" rhodium-sulphide complexes are comparable in activity with homogeneous systems, such as for example the homogeneous rhodium-phosphine complex RhCl[P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>]<sub>3</sub>, but above all have the advantage over homogeneous systems of a much longer service life and are easier to separate from other constituents of the reaction mixture, such as solvent, substrate or product.

The "heterogenised" catalysts according to the invention may be isolated from the reaction medium by decantation, centrifuging or filtration and re-used without any loss of activity and without even the slightest trace in the dissolved phase of rhodium-containing compounds.

By virtue of the presence of two silicon atoms per ligand L and with suitable functionalisation, the "heterogenisable" monomeric catalysts according to the invention allow both intramolecular and also intermolecular condensation reactions, whereby it is possible in conjunction with the condensation conditions selected to influence the particle structure of a polymer to be produced by heterogenisation.

Where heterogenisation is carried out by fixing to a support, the nature of the functionalisation on both silicon atoms enables the physical behaviour of the solids with respect to solvents or constituents of reaction mixtures to be influenced, so that it is possible for example to adjust any desired suspendability or wettability level in media such as these.

The invention is illustrated by the following Examples. The special sulphide ligands L corresponding to formula 1 used in accordance with the invention in the systems RhX<sub>3</sub>L<sub>3</sub> and RhCl(CO)L<sub>2</sub> in these Examples are simple and readily obtainable representatives of their type and, hence, have a model character. This claim is justified in particular by the generally known properties of organosilicon compounds of this type and also by the fact that the sulphide ligands of the new rhodium complexes are not significantly different in their ligand qualities, i.e. the co-ordination capacity of the sulphur atom, from the prior art discussed at the beginning (German Offenlegungsschrift Nos. 2,453,229; 2,405,274 and 2,550,660). Accordingly, analogy to other species L suitable for use in accordance with the invention is justified because it is obvious to any expert. Naturally, the same also applies to the anion X used.

#### EXAMPLE 1

0.935 g (2.81 mmoles) of RhCl<sub>3</sub>(CH<sub>3</sub>CN)<sub>3</sub> and 3.85 g (9.28 mmoles) of S[(CH<sub>2</sub>)<sub>2</sub>Si(OC<sub>2</sub>H<sub>5</sub>)<sub>3</sub>]<sub>2</sub> were combined in 60 ml of dry toluene and the solution was heated under reflux for 16 hours in an atmosphere of purified and dried nitrogen. The solution was then filtered off and the solvent distilled off *in vacuo*. The residual oil was taken up in 40 ml of warm, dry *n*-pentane and crystallised out at temperatures of <-80°C. This operation was then repeated. After drying at 50°C/10<sup>-2</sup> mbars, 3.95 g (96.6% of the theoretical, based on RhCl<sub>3</sub>(CH<sub>3</sub>CN)<sub>3</sub>) of RhCl<sub>3</sub>[S[(CH<sub>2</sub>)<sub>2</sub>Si(OC<sub>2</sub>H<sub>5</sub>)<sub>3</sub>]<sub>2</sub>]<sub>3</sub> were obtained in the form of an orange-red, viscous oil.

Analyses:	C%	H%	Cl%	S%	Rh%
calculated:	39.67	7.91	7.32	6.62	7.08
observed:	39.33	7.55	7.52	6.18	6.88

The composition was confirmed by IR- and NMR-spectroscopy.

#### EXAMPLE 2

0.875 g (2.63 mmoles) of RhCl<sub>3</sub>(CH<sub>3</sub>CN)<sub>3</sub> and 3.11 g (8.67 mmoles) of S[(CH<sub>2</sub>)<sub>3</sub>Si(OCH<sub>3</sub>)<sub>3</sub>]<sub>2</sub> were combined in 60 ml of dry toluene and the solution stirred for 20 hours at reflux temperature in a

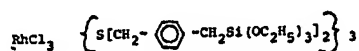
nitrogen atm sph re. Insoluble constituents of the mixture were then filtered off and the solvent was distilled off *in vacuo*. The oily residu was taken up in warm, dry *n*-hexane and crystallised out in a bath of dry ice and methanol. The purification step was repeated and the orange-red viscous oil obtained was dried at 50°C/10<sup>-2</sup> mbar. RhCl<sub>3</sub>{S[(CH<sub>2</sub>)<sub>3</sub>Si(OCH<sub>3</sub>)<sub>3</sub>Si(OCH<sub>3</sub>)<sub>3</sub>]<sub>2</sub>]<sub>3</sub> was isolated in a yield of 3.32 g (98.2% of the theoretical based on RhCl<sub>3</sub>(CH<sub>3</sub>CN)<sub>3</sub>).

Analyses:	C%	H%	Cl%	S%	Rh%
calculated:	33.65	7.06	8.28	7.48	8.01
observed:	33.45	6.87	8.82	7.08	7.53

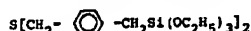
The composition was confirmed by IR- and NMR-spectroscopy.

#### 10 EXAMPLE 3

Following the procedure of Example 2, 4.437 g (96.0% of the theoretical, based on RhCl<sub>3</sub>(CH<sub>3</sub>CH)<sub>3</sub>) of



were obtained from 0.804 g (2.42 mMoles) of RhCl<sub>3</sub>(CH<sub>3</sub>CN)<sub>3</sub> and 4.53 g (7.99 mMoles) of



Analyses:	C%	H%	Cl%	S%	Rh%
calculated:	17.61	2.43	5.57	5.04	5.39
observed:	17.46	2.60	5.38	5.06	5.22

The substance was further identified by IR- and NMR-spectroscopy. Both spectra are characterised by the bands of the sulphide ligands.

#### EXAMPLE 4

9.54 g (23.0 mMoles) of S[(CH<sub>2</sub>)<sub>2</sub>Si(OC<sub>2</sub>H<sub>5</sub>)<sub>3</sub>]<sub>2</sub>, dissolved in 20 ml of dry *n*-hexane, were added dropwise over a period of 20 minutes to a boiling solution of 2.13 g (5.48 mMoles) of [Rh(CO)<sub>2</sub>Cl]<sub>2</sub> in 80 ml of dry *n*-hexane and the resulting mixture was heated under reflux in a nitrogen atmosphere for another three days, during which the reaction was monitored by IR-spectroscopy (characteristic νCO-vibrations). The product was filtered off and crystallised out at temperatures < -78°C. After reconcentration by freezing from 50 ml of *n*-pentane, followed by drying at 50°C/10<sup>-2</sup> mbars, 10.4 g (95.3% of the theoretical) of RhCl(CO) {S[(CH<sub>2</sub>)<sub>2</sub>Si(OC<sub>2</sub>H<sub>5</sub>)<sub>3</sub>]<sub>2</sub>} were obtained in the form of an oil yellow-green in colour after dilution.

Analyses:	C%	H%	Cl%	S%	Rh%
calculated:	39.80	7.69	3.56	6.44	10.33
observed:	38.50	6.97	3.36	6.45	9.94

The substance was further identified by IR-and NMR-spectroscopy.

IR-spectrum: ν CO  
pressing KBr 1967 cm<sup>-1</sup> (sst)  
solution *n*-hexane 1973, 1983 cm<sup>-1</sup> (sst).

#### EXAMPLE 5

8.20 g (22.87 mMoles) of S[(CH<sub>2</sub>)<sub>3</sub>Si(OCH<sub>3</sub>)<sub>3</sub>]<sub>2</sub>, dissolved in 20 ml of *n*-hexane, were added dropwise over a period of 15 minutes to a boiling solution of 2.10 g (5.40 mMoles) of [Rh(CO)<sub>2</sub>Cl]<sub>2</sub> in 80 ml of *n*-hexane and the resulting mixture heated under reflux for another three days in a nitrogen atmosphere. The product was filtered off and crystallised at -78°C (CO<sub>2</sub>/methanol). After the oil obtained had been taken up again in 50 ml of *n*-hexane, followed by reconcentration by freezing and drying at 50°C/10<sup>-2</sup>mbar, 9.40 g (98.5% of the theoretical) of RhCl(CO){S[(CH<sub>2</sub>)<sub>3</sub>Si(OCH<sub>3</sub>)<sub>3</sub>]<sub>2</sub>} were obtained in the form of an oil greenish-yellow in colour after dilution.



Analyses:	C%	H%	Cl%	S%	Rh%
calculated:	33.98	6.84	4.01	7.26	11.65
observed:	33.91	6.54	4.31	7.27	12.73

The substance was further identified by IR- and NMR-spectroscopy.

5

IR-spectrum:  $\gamma$ CO

5

pressing KBr 1965  $\text{cm}^{-1}$  (sst)

Solution *n*-hexane 1970, 1980  $\text{cm}^{-1}$  (sst).

#### EXAMPLES 6 to 12

- General procedure for "heterogenising" various compounds of the  $\text{RhCl}_3\text{L}_3$ -type by polymerisation: 10
- $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$  was first dissolved in warm ethanol. The calculated quantity of silicon-containing sulphide compound was added to the resulting solution and the mixture stirred under reflux for about 2 to 3 hours. The solvent was then distilled off, leaving a dark-red oily residue behind in the flask. This residue was taken up in hot toluene and stirred until a clear solution was obtained. An excess quantity of water was then slowly added dropwise under heat. 15
- A voluminous, more or less brightly orange coloured solid was precipitated after only the first few drops. After stirring under reflux for at least another 2 hours, first a toluene/ethanol/ $\text{H}_2\text{O}$ -azetrope and then a toluene/ $\text{H}_2\text{O}$ -azetrope were separated off on a water separator. After more toluene had been added, followed by filtration under heat, the residual solid was extracted with hot toluene and ethanol in a Soxhlet apparatus for a total of 24 hours and dried at  $100^\circ\text{C}/10^{-2}$  mbars. The filtrates or extracts 20
- were in general substantially colourless, which is indicative of a substantially quantitative precipitation of the rhodium-sulphide complexes. 20

In Example 10, tetraethyl silicate was used as the crosslinker. It was added to the reaction solution shortly before hydrolysis.

Example No.	Starting substances rhodium component (g) (mMoles)		sulphide component (g) (mMoles)	
6	$\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ 1.08	4.11	$\text{S}[(\text{CH}_2)_3\text{Si}(\text{OC}_2\text{H}_5)_3]_2$ 5.96	14.37
7	$\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ 0.57	2.17	$\text{S}[(\text{CH}_2)_3\text{Si}(\text{OC}_2\text{H}_5)_3]_2$ 5.39	13.00
8	$\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ 0.895	3.40	$\text{S}[(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3]_2$ 4.26	11.88
9	$\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ 1.53	5.80	$\text{S}[(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3]_2$ 12.50	34.86
10	$\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ 1.46	5.54	$\text{S}[(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3]_2$ 7.00 $\text{Si}(\text{OC}_2\text{H}_5)_4$ 8.13	19.52 39.02
11	$\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ 1.43	5.43	$\text{S}[(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3]_2$ 7.89	19.02
12	$\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ 1.40	5.32	$\text{S}[\text{CH}_2 - \text{C}_6\text{H}_4 - \text{CH}_2\text{Si}(\text{OC}_2\text{H}_5)_3]_2$ 9.95	17.55

Example No.	Solvent		H <sub>2</sub> O (ml)	Yield, based on total weighed portion (g) (%) <sup>a</sup>	
	ethanol (ml)	toluene (ml)			
6	50	50 + 50	5	3.53	97.4
7	50	50 + 50	5	2.90	98.2
8	50	50 + 50	4	2.328	100
9	50	50 + 20	8	8.85	99.5
10	50	50 + 50	8	8.34	106.8
11	60	50 + 50	5	6.38	99.7
12	60	50 + 50	5	7.05	98.5

<sup>a</sup>Based on the quantity of precipitated product expected in the event of complete hydrolysis.

Example No.	Product analyses					
		Rh (%)	Cl (%)	S (%)	C (%)	H (%)
6	calc.	11.68	12.05	12.72	19.06	3.20
	obs.	12.18	10.96	11.43	19.35	3.65
7	calc.	7.55	7.80	14.11	21.14	3.55
	obs.	7.60	8.13	13.20	20.68	3.74
8	calc.	10.50	10.85	11.44	25.72	4.32
	obs.	9.35	10.96	11.01	25.30	4.56
9	calc.	6.71	6.93	12.56	28.24	4.74
	obs.	5.75	7.05	12.17	29.05	4.87
10	calc.	7.30	7.55	8.02	18.02	3.02
	obs.	6.80	7.03	7.79	18.08	3.86
11	calc.	8.74	9.03	9.53	35.72	6.00
	obs.	8.02	8.74	9.01	35.90	6.44
12	calc.	7.65	7.90	7.86	47.11	3.95
	obs.	7.44	8.11	7.71	47.85	4.36

#### EXAMPLE 13

1.5 g (4.15 mMoles) of  $\text{RhCl}_3(\text{CH}_3\text{CN})_3$  and 8.03 g (22.50 mMoles) of  $\text{S}[\text{CH}_2\text{CH}_2\text{SiCl}_3]_2$  were combined in 60 ml of dry toluene and the resulting solution stirred under reflux for 10 hours. Traces of substantially insoluble constituents were then filtered off from the reaction mixture and 8 ml of water were added dropwise to the filtrate. After the resulting suspension had been refluxed for another 2 hours, aqueous HCl-solution, the acetonitrile liberated and some of the toluene were distilled off, 50 ml of fresh toluene were added and the orange-colored solid was filtered off, followed by extraction with ethanol for 8 hours in a Soxhlet apparatus. After drying for 3 hours at  $110^\circ\text{C}/10^{-2}$  mbars, 5.1 g (96.7% of the theoretical) product were obtained.

The following analytical values were calculated for complete hydrolysis and precipitation:

C%	H%	Rh%	Cl%	S%
20.51	3.44	8.80	9.10	13.68

The following values were observed:

C%	H%	Rh%	Cl%	S%
20.10	3.09	8.39	10.22	13.20

#### EXAMPLE 14

34.89 g (97.3 mMoles) of  $\text{S}[(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3]_2$  were added to a clear solution of 0.256 g (0.973 mMoles) of  $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$  in 80 ml of dried ethanol, followed by heating for 2 hours to boiling temperature. The solvent was distilled off and the oily residue was taken up in 50 ml of dry toluene. This solution was transferred to a dropping funnel and added dropwise over a period of about 1 hour to 40 ml of a hot 2N HCl-solution. The deposit formed was vigorously stirred for another 4 hours at 100°C. The alcohol formed and the aqueous HCl solution were then removed from the reaction mixture by distillation. After the addition of another 50 ml of toluene, the solid was filtered off, extracted with toluene and ethanol in a Soxhlet apparatus (for a total of 24 hours) and dried for 3 hours at 110°C/10<sup>-2</sup> mbar. 19.49 g (90.0% of the theoretical) of a yellow powder were obtained.

The following analytical values were calculated for complete elimination of the alcohol and quantitative precipitation:

C%	H%	Rh%	Cl%	S%
32.39	5.44	0.463	0.478	14.41

The following analytical values were observed:

C%	H%	Rh%	Cl%	S%
30.03	5.56	0.49	0.87	12.8

#### EXAMPLES 15 to 23

General procedure for fixing various compounds of the  $\text{RhCl}_3\text{L}_3$ -type (L = sulphide ligand corresponding to formula (1)) to inorganic supports containing acid OH-groups:

The calculated quantities of  $\text{RhCl}_3(\text{CH}_3\text{CN})_3$  and sulphide component were combined in 50 ml of dry toluene and the solution stirred under reflux for between three and twelve hours, depending on the sulphide content. The solution was then transferred to a dropping funnel and added dropwise over a period of 15 minutes to a vigorously stirred suspension of 20 g of dried support material in 250 ml of toluene. After stirring under reflux for another 48 hours, the solvent was removed by distillation, the generally pale orange coloured product remaining in the flask was transferred to an extraction shell, extracted with toluene for 24 hours and then dried at 110°C/10<sup>-2</sup> mbar. General procedure for fixing various compounds of the  $\text{RhCl}(\text{CO})\text{L}_2$ -type (L = sulphide ligand corresponding to formula (1)) to inorganic supports containing acid OH-groups:

The calculated quantities of  $[\text{Rh}(\text{CO})_2\text{Cl}]_2$  and sulphide component were combined in 40 ml of dry n-hexane and the solution stirred under reflux for between 2 and 3 days, depending on the sulphide content. Thereafter the procedure was as described above, except that n-hexane was used instead of toluene. The reaction time with the support material was increased to 60 hours.

Example No.	Starting substances	
	rhodium compound (mg) (mMoles)	sulphide component (mg) (mMoles)
15	$\text{RhCl}_3(\text{CH}_3\text{CN})_3$ 166.21 0.5	$\text{Si}[(\text{CH}_2)_3\text{Si}(\text{OC}_2\text{H}_5)_3]_2$ 622.06 1.5
16	$\text{RhCl}_3(\text{CH}_3\text{CN})_3$ 166.21 0.5	$\text{Si}[(\text{CH}_2)_3\text{Si}(\text{OC}_2\text{H}_5)_3]_2$ 1451.5 3.5
17	$\text{RhCl}_3(\text{CH}_3\text{CN})_3$ 166.21 0.5	$\text{Si}[(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3]_2$ 537.9 1.5
18	$\text{RhCl}_3(\text{CH}_3\text{CN})_3$ 166.21 0.5	$\text{Si}[(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3]_2$ 896.5 2.5
19	$\text{RhCl}_3(\text{CH}_3\text{CN})_3$ 166.21 0.5	$\text{Si}[(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3]_2$ 896.5 2.5
20	$\text{RhCl}_3(\text{CH}_3\text{CN})_3$ 166.21 0.5	$\text{Si}[(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3]_2$ 2689.5 7.5
21	$\text{RhCl}_3(\text{CH}_3\text{CN})_3$ 332.42 1.0	$\text{Si}[(\text{CH}_2)_3\text{Si}(\text{C}_6\text{H}_5)_2\text{OC}_2\text{H}_5]_2$ 1712.82 2.0
22	$\text{RhCl}_3(\text{CH}_3\text{CN})_3$ 166.21 0.5	$\text{Si}[(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3]_2$ 896.5 2.5
23	$[\text{Rh}(\text{CO})_2\text{Cl}]_2$ 97.19 0.25	$\text{Si}[(\text{CH}_2)_3\text{Si}(\text{OC}_2\text{H}_5)_3]_2$ 414.7 1.0

Example No.	Reaction time (h)	Support material
15	12	Aerosil 200 0.6 mMole SiOH/g
16	3	Aerosil 200 0.6 mMole SiOH/g
17	12	Aerosil 200 0.6 mMole SiOH/g
18	8	Aerosil 200 0.6 mMole SiOH/g
19	8	Ultrasil VN 3 1.2 mMole SiOH/g
20	3	Ultrasil VN 3 1.2 mMole SiOH/g
21	12	Ultrasil VN 3 1.2 mMole SiOH/g
22	9	titanium dioxide P25
23	72	Aerosil 200 0.6 mMole SiOH/g

"Aerosil" and "Ultrasil" are Trade Marks.

Example No.	Product Analyses			
		Rh (%)	Cl (%)	S (%)
15	calc.	0.254	0.263	0.237
	obs.	0.20	0.30	0.23
16	calc.	0.25	0.258	0.544
	obs.	0.26	0.34	0.49
17	calc.	0.252	0.26	0.235
	obs.	0.23	0.33	0.23
18	calc.	0.25	0.26	0.39
	obs.	0.18	0.30	0.40
19	calc.	0.25	0.26	0.39
	obs.	0.23	0.33	0.47
20	calc.	0.24	0.25	1.12
	obs.	0.24	0.35	1.09
21	calc.	0.475	0.49	0.44
	obs.	0.46	0.48	0.52
22	calc.	0.25	0.26	0.39
	obs.	0.24	0.30	0.36
23	calc.	0.25	0.09	0.16
	obs.	0.28	0.12	0.17

## EXAMPLE 24

7 ml of a 35% aqueous  $\text{CH}_2\text{O}$ -solution diluted with 10 ml of ethanol were added dropwise over a period of 15 minutes to a suspension of 3 g of the "heterogenised" rhodium-sulphide complex produced in accordance with Example 9 in 50 ml of boiling ethanol, after which the mixture was stirred under reflux for another hour. A solution of 0.7 g of  $\text{NaBH}_4$  in 30 ml of ethanol was then added over a period of about 10 minutes, followed by stirring under reflux for another hour. The solid was then filtered off, extracted with ethanol for 2 hours in a Soxhlet apparatus and, finally, dried for 3 hours at  $100^\circ\text{C}/10^{-2}$  mbar. As a result of this treatment, the previously orange coloured solid assumed a yellow-green colour. Yield: 2.9 g.

When the product (in the form of a KI pressing) was analysed by IR-spectroscopy, a new band was observed at  $1967\text{ cm}^{-1}$  which, very probably, is a  $\nu\text{CO}$ -vibration.

## EXAMPLE 25.

0.988 g of a solid containing rhodium-sulphide complex produced in accordance with Example 14 (rhodium content 5.3%, chlorine content 8.03% and S-content 9.77) were suspended in 40 ml of boiling ethanol, followed by the addition over a period of 20 minutes with vigorous stirring of a solution of 313 mg of  $\text{NaBH}_4$  in 25 ml of ethanol. After stirring under reflux for another 2 hours, the solid which, in the meantime, had changed from orange to yellow-green in colour was filtered off, extracted with ethanol for 4 hours in a Soxhlet apparatus and dried for 2.25 hours at  $110^\circ\text{C}/10^{-2}$  mbar.

## EXAMPLE 26

0.48 ml of a 35% aqueous formaldehyde solution diluted with 10 ml of ethanol was added over a period of 15 minutes to a boiling suspension of 10 g of the support-fixed rhodium complex produced in accordance with Example 19 in 150 ml of ethanol, after which the mixture was stirred under reflux for another hour. Thereafter a solution of 45.5 mg of  $\text{NaBH}_4$  in 30 ml of ethanol was added dropwise over a period of 10 minutes, followed by heating under reflux for another 2 hours. After the solid had been filtered off, extracted with ethanol for 4 hours and dried at  $100^\circ\text{C}/10^{-2}$  mbar, some of the 9.5 g of catalyst obtained was used for hydrogenating crotonic acid (Example 33).

## EXAMPLE 27

A mixture of 422 mg of the rhodium-sulphur compound (12.18% Rh) produced in accordance with Example 6, 62.5 ml of 1-hexene and 180 ml of toluene was exposed to a cold CO/H<sub>2</sub>-pressure (1:1) of 200 bars in a 500 ml lift autoclave. Approximately 97% of the 1-hexene used reacted over a period of 10 minutes at a temperature of 135°C to form *n*-heptanal and 2-methyl hexanal. The reaction mixture was found by gas chromatography to consist of approximately 47% of *n*-heptanal, approximately 50% of 2-methyl hexanal and approximately 3% of 1-hexene/*n*-hexene.

For further use, the undissolved catalyst was filtered off from the liquid phase and washed with toluene.

## EXAMPLE 28

In a 500 ml lift autoclave, 62.5 ml of 1-hexene dissolved in 180 ml of toluene were hydroformylated over a period of 14 minutes at a temperature of 120°C under a cold CO/H<sub>2</sub>-pressure (1:1) of 200 bars using the separated catalyst of Example 27. The pressure loss which occurred was compensated by the introduction of more CO and H<sub>2</sub> under pressure. Another 62.5 ml of 1-hexene were pumped into the autoclave by means of a metering pump. The temperature was kept at 120°C. The uptake of H<sub>2</sub>/CO occurred over a period of 22 minutes. After the pressure loss had been compensated again and after another 62.5 ml of 1-hexene had been pumped in, the uptake of gas stopped after only 10 minutes. The autoclave was cooled and vented. Analysis of the reaction mixture by gas chromatography showed that 98% of the 1-hexene had undergone hydroformylation, approximately 53% of *n*-heptanal and approximately 47% of 2-methyl hexanal having been formed. It was not possible to detect even the slightest traces of the corresponding alcohols.

## EXAMPLE 29

Using 677 mg of the catalyst obtained in accordance with Example 7 (7.60% Rh), 62.5 ml of 1-hexene were reacted over a period of 40 minutes at a temperature of 115°C and under a total cold H<sub>2</sub>/CO-pressure (1:1) of 200 bars to form *n*-heptanal and 2-methyl hexanal in a conversion of more than 97%. The reaction mixture was found by gas chromatography to contain approximately 53% of straight-chain aldehyde, approximately 44% of aldehyde and approximately 3% of 1-Hexene/hexane.

## EXAMPLE 30

On completion of the reaction according to Example 29, the catalyst used was filtered off, washed with toluene and reused for the hydroformylation of, initially 62.5 ml of 1-hexene. After a CO-pressure of 100 bars and an H<sub>2</sub>-pressure of 100 bars had been set up, hydroformylation was carried out under a total pressure of 230 to 190 bars, but at a temperature of 180°C. After another 2 x 62.5 ml of 1-hexene had been introduced, the total starting pressure being restored to 230 bars, analysis by gas chromatography showed that, after a total reaction time of 9 hours, the 1-hexene used had been converted into 2-methyl hexanol (58%), *n*-heptanol (37%) and hexane (5%).

## EXAMPLE 31

62.5 ml of 1-hexene and 441.8 g of RhCl(CO){S[(CH<sub>2</sub>)<sub>3</sub>Si(OCH<sub>3</sub>)<sub>3</sub>]<sub>2</sub>}<sub>2</sub> produced by reacting [Rh(CO)<sub>2</sub>Cl]<sub>2</sub> with S[(CH<sub>2</sub>)<sub>3</sub>Si(OCH<sub>3</sub>)<sub>3</sub>]<sub>2</sub> in accordance with Example 5, were dissolved in 180 ml of toluene and exposed to a cold H<sub>2</sub>/CO-pressure (1:1) of 200 bars. Approximately 99% of the 1-hexene reacted to form the isomeric aldehydes over a period of 10 minutes at a temperature of 100°C. Analysis by gas chromatography showed that the isomer distribution was approximately 53% of *n*-heptanal and 47% of 2-methyl hexanal.

## EXAMPLE 32

The solid treated in accordance with Example 24 was used for the hydrogenation of ethylacrylate. To this end, 68 mg of the catalyst were combined with 8.70 ml of ethylacrylate in a 50 ml flask which was connected to a hydrogenation apparatus. With magnetic stirring, under a hydrogen pressure of approximately 1 bar and at a temperature of 80°C ± 2°C, the ethylacrylate used was quantitatively reacted to form ethyl propionate over a period of 230 minutes, as shown by the amount of hydrogen taken up and by analysis of the reaction product by gas chromatography. The average uptake of hydrogen amounted to 8.4 ml/minute. A first batch of 4.35 ml of ethylacrylate was then sprayed into this catalyst suspension. On completion of the reaction, further 4.35 ml batches (40 mMoles) of ethylacrylate were sprayed in in order to determine both the activity of the catalyst and, at the same time, its useful life in dependence upon the filling level of the flask. The following Table shows the reaction time required and the average uptake of hydrogen per minute observed.

Hydrogenation No.	Average H <sub>2</sub> uptake rate (ml/minute)	Reaction time (mins)
2	8.8	110
3	12.1	79
4	14.2	68
5	16.5	59
6	14.6	66

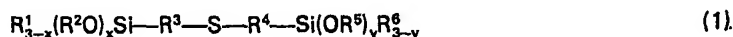
After this hydrogenation series, the catalyst was filtered off from the clear colourless solution, washed with 2 × 10 ml of toluene, dried at 100°C/10<sup>-2</sup> mbar and used for a second hydrogenation series according to the same programme. The data observed in the first series were reproduced. After the quantitative hydrogenation of 0.6 mole of ethylacrylate to form ethyl propionate, these tests were terminated without any sign of the catalyst used having been deactivated.

#### EXAMPLE 33

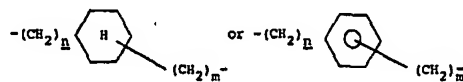
823 mg of the catalyst treated in accordance with Example 26 were added to a solution of 1.722 g of crotonic acid in 20 ml of toluene and the 50 ml flask used was connected to a hydrogenation apparatus. With magnetic stirring at a temperature of 80°C ± 2°C and under a hydrogen pressure of approximately 1 bar, the crotonic acid used was quantitatively hydrogenated into butyric acid over a period of 110 minutes, as shown by the amount of H<sub>2</sub> taken up (485 ml) and analysis of the reaction solution by gas chromatography.

#### CLAIMS:

1. Complex compounds of rhodium in which at least one sulphide corresponding to the general formula



- is co-ordinatively bound to the central atom, its still free co-ordination sites, if any being occupied by carbon monoxide, an olefin, amine, phosphine or nitrile and a necessary charge exchange with a chloride, bromide or iodide ion, an acetate, trifluoroacetate or propionate ion having been completed, optionally with complete or partial replacement of these anions by a hydride ion; in formula (1), R<sup>1</sup> and R<sup>6</sup> representing a straight-chain or branched alkyl group containing from 1 to 5 carbon atoms, a cycloalkyl radical containing from 5 to 8 carbon atoms, a benzyl or phenyl radical optionally substituted by one or more methyl, ethyl propyl, methoxy, ethoxy groups, NO<sub>2</sub>-groups halide or cyanide and also chloride or bromide, R<sup>2</sup> and R<sup>5</sup> representing a straight-chain or branched alkyl group containing from 1 to 5 carbon atoms, a cycloalkyl group containing from 5 to 8 carbon atoms, an optionally substituted phenyl or benzyl group or a 2-methoxyethyl or 2-ethoxyethyl group, R<sup>2</sup> and R<sup>5</sup> being the same or different, R<sup>3</sup> and R<sup>4</sup> representing a straight-chain or branched alkylene group containing from 1 to 10 carbon atoms, a phenylene or cycloalkylene group containing from 5 to 8 carbon atoms optionally substituted by a methyl, ethyl, propyl or iso-propyl group and units of the type



- where n and m may be a number of from 0 to 5 and the ring H-atoms may be partly replaced by halogen, particularly F, Cl, Br, or a cyanide group, R<sup>3</sup> and R<sup>4</sup> being the same or different, and x and y may be the number 1, 2 or 3 or may be 0 when R<sup>1</sup> or R<sup>6</sup> represents chlorine or bromine, x and y being the same or different.

2. Complex compounds as claimed in Claim 1 having the stoichiometric composition



in which sulphide compounds corresponding to formula (1) are present as ligands L and X represents chlorine, bromine, iodine, acetate, trifluoroacetate or propionate.

3. Complex compounds as claimed in Claim 2, wherein they are aftertreated with H<sub>2</sub> and CO in a



solvent, such as benzene, toluene, xylene, *n*-hexane, cyclohexane, methyl cyclohexane, monoglyme, diethyl ether, tetrahydrofuran, dioxane and, in particular, lower alcohols under total pressures of from 10 to 300 bars and at temperatures in the range of from 50 to 200°C.

4. Complex compounds as claimed in Claim 1 having the stoichiometric composition

5  $\text{RhCl}(\text{CO})\text{L}_2$  5

in which sulphide compounds corresponding to formula (1) are present as ligands L.

5. A process for producing the complex compounds claimed in Claim 2, wherein sulphides corresponding to general formula (1) are reacted with anhydrous rhodium compounds representing salts of hydrohalic acid or a lower organic carboxylic acid and optionally containing readily displaceable ligands, preferably lower aliphatic nitriles or benzonitrile.

6. A process as claimed in Claim 5, wherein the complex compounds are aftertreated with hydrogen and carbon monoxide in a solvent, such as benzene, toluene, xylene, *n*-hexane, cyclohexane, methyl cyclohexane, monoglyme, diethyl ether, tetrahydrofuran, dioxane and, in particular, lower alcohols under total pressures of from about 10 to 300 bars and at temperatures in the range from 50 to 200°C.

7. A process for producing the complex compounds claimed in Claim 4 wherein sulphides corresponding to general formula (1) are reacted with  $[\text{Rh}(\text{CO})_2\text{Cl}]_2$  at a temperature below 100°C.

8. A process as claimed in Claim 5 or 7, wherein the reaction is carried out in an apolar or polar inert and anhydrous solvent, such as benzene, toluene, *n*-hexane, *n*-pentane, cyclohexane, methyl cyclohexane, petroleum ether, methanol, ethanol, propanol, isopropanol, di-ethyl ether, tetrahydrofuran, monoethylene glycol dimethyl ether, acetone, at temperatures between room temperature and the boiling temperature of the solvent.

9. Polymeric compounds having a silica-like structure and the function of a rhodium support which are sparingly soluble in organic solvents and to which rhodium salts or a hydrohalic acid or a lower organic carboxylic acid optionally containing carbon monoxide olefin, amine, phosphine or nitrile ligands are co-ordinatively bound through at least one L', L' representing a sulphide compound L with trifunctionally substituted silicon corresponding to formula (1) as defined in claim 1, in which the groups  $\text{OR}^2$  and  $\text{OR}^5$ ,  $\text{R}^1$  and  $\text{R}^6$  originally present — the latter preferably in the form of chlorine or bromine ions — are partly or completely split off hydrolytically as alcohol or phenol, HCl or HBr and in which a ratio of rhodium to sulphide of from 1:1 to 1:10<sup>6</sup> is present, obtained by reacting complex compounds having the stoichiometric composition  $\text{RhX}_3\text{L}_3$ , in which L represents at least one ligand corresponding to formula (1) as defined in claim 1 and carbon monoxide, olefin, amine, phosphine or nitrile bound to still free co-ordination sites, if any, and X is as defined in Claim 2, with water or an aqueous acid solution, optionally in the presence of an excess of the sulphide L over and above the stoichiometric composition  $\text{RhX}_3\text{L}_3$  and/or in the presence of crosslinking agents, such as methyl or ethyl silicate, optionally with removal of alcohol or phenol formed by distillation, or by reacting the ligand L with water or an aqueous acid solution, optionally in presence or crosslinking agents of the above-mentioned type and optionally with removal of alcohol or phenol formed by distillation, and reacting the solid formed with rhodium compounds representing aqueous or anhydrous salts of hydrohalic acid or a lower carboxylic acid and optionally containing readily displaceable ligands, preferably lower aliphatic nitriles or benzonitrile, or with the compound  $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ .

10. A process for producing the polymers claimed in Claim 9, wherein complex compounds having the stoichiometric composition  $\text{RhX}_3\text{L}_3$ , in which L represents at least one ligand of formula (1) as defined in claim 1 provided with trifunctionally substituted silicon and carbon monoxide, olefin, amine, phosphine or nitrile bound to still free co-ordination sites, if any, and X is as defined in Claim 2, are reacted with water or an aqueous acid solution, optionally in the presence of an excess of the sulphide L over and above the stoichiometric composition  $\text{RhX}_3\text{L}_3$  and/or in the presence of crosslinking agents, such as methyl or ethyl silicate, optionally with removal of alcohol or phenol formed by distillation, or the ligand L is reacted with water or an aqueous acid solution, optionally in the presence of crosslinking agents of the above-mentioned type and optionally with removal of alcohol or phenol formed by distillation, and the solid formed is reacted with rhodium compounds representing aqueous or anhydrous salts of a hydrohalic acid or a lower carboxylic acid and optionally containing readily displaceable ligands, preferably lower aliphatic nitriles or benzonitrile, or with the compound  $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ .

11. A process as claimed in Claim 10, characterised in that a rhodium compound from the series  $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ ,  $\text{RhBr}_3 \cdot 2\text{H}_2\text{O}$ ,  $\text{RhI}_3$ ,  $\text{RhCl}_3(\text{CH}_3\text{CN})_3$ ,  $\text{RhCl}_3(\text{C}_2\text{H}_5\text{CN})_3$ ,  $\text{RhCl}_3(\text{C}_6\text{H}_5\text{CN})_3$ ,  $\text{RhBr}_3(\text{CH}_3\text{CN})_3$  or other rhodium systems containing readily substitutable ligands, is reacted with the required quantity of sulphide compound L in pure substance or in solution to form the complex compound  $\text{RhX}_3\text{L}_3$  which, optionally after the solvent has been changed to avoid a back reaction, i.e. after ethanol has been replaced by toluene for example, is hydrolysed by precipitation with water or an aqueous acid solution, optionally with removal of alcohol or phenol formed by distillation.

12. Complex rhodium compounds bound through inorganic supports containing surface oxygen atoms, of the type



in which X is as defined in Claim 2 and L represents at least one ligand corresponding to formula (1) as defined in claim 1 and carbon monoxide, olefin, amine, phosphine or nitrile bound to still free coordination sites, if any, through which the bond with the support is established by reaction of the acid hydrogen with the groups  $\text{OR}^2$  and  $\text{OR}^3$ ,  $\text{R}^1$  and  $\text{R}^6$  originally present — the latter preferably in the form of chlorine or bromine ions, with elimination of alcohol or phenol,  $\text{HCl}$  or  $\text{HBr}$ , any still unco-ordinated residues of the sulphide being bound to the support and rhodium:sulphide ratios of from 1:1 to 1:10<sup>3</sup> being present, obtained by treating a solution of the compound  $\text{RhX}_3\text{L}_3$  or  $\text{RhCl}(\text{CO})\text{L}_2$  with a suspension of the support material in an inert organic solvent, optionally in the presence of excess sulphide L of formula (1) within the quantitative ratio limits specified, at temperatures between room temperature and the reflux temperature of the suspending agent used, or by treating a sulphide of formula (1) with a suspension of the support material in an inert organic solvent under the temperature conditions specified and subsequently reacting the solid form with rhodium compounds representing anhydrous or aqueous salts of a hydrohalic acid or a lower carboxylic acid and optionally containing readily displaceable ligands, preferably lower aliphatic nitriles or benzonitrile, or with the compound  $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ .

13. Support-fixed complex rhodium compounds as claimed in Claim 12, wherein the support is pyrogenic or precipitated silica, quartz, a silicate-containing glass, silica gel, titanium dioxide, zirconium dioxide, a zeolite, aluminium oxide, kaolin, bauxite, diatomaceous earth or another substance containing acid OH-groups synthesised from oxide compounds of aluminium and silicon and salts or oxides of other metals.

14. A process for producing the support-fixed rhodium compounds claimed in Claims 12 and 13, wherein a solution of the compound  $\text{RhX}_3\text{L}_3$  or  $\text{RhCl}(\text{CO})\text{L}_2$  is treated with a suspension of the support material in an inert organic solvent, optionally in the presence of excess sulphides corresponding to formula (1) at temperatures between room temperature and the reflux temperature of the suspending agent used, or a sulphide corresponding to formula (1) is treated with a suspension of the support material in an inert organic solvent under the specified temperature conditions, after which the solid formed is reacted with rhodium compounds representing anhydrous or aqueous salts of a hydrohalic acid or a lower carboxylic acid and optionally containing readily displaceable ligands, preferably lower aliphatic nitriles or benzonitrile, or with the compound  $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ .

15. A process as claimed in Claim 14, wherein a rhodium compound of the series  $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ ,  $\text{RhBr}_3 \cdot 2\text{H}_2\text{O}$ ,  $\text{RhI}_3$ ,  $\text{RhCl}_3(\text{CH}_3\text{CN})_3$ ,  $\text{RhCl}_3(\text{C}_2\text{H}_5\text{CN})_3$ ,  $\text{RhCl}_3(\text{C}_6\text{H}_5\text{CN})_3$ ,  $\text{RhBr}_3(\text{CH}_3\text{CN})_3$  and  $[\text{Rh}(\text{CO})_2\text{Cl}]_2$  or other rhodium systems containing readily substitutable ligands, is reacted with the required quantity of sulphide compound L in pure substance or in solution to form the complex compound  $\text{RhX}_3\text{L}_3$  or  $\text{RhCl}(\text{CO})\text{L}_2$  which is then treated with a suspension of the support material, optionally after the solvent has been changed to avoid a back reaction, i.e. after ethanol has been replaced by toluene for example.

16. A process as claimed in Claim 14 and 15, wherein benzene, toluene, xylene, cyclohexane or *n*-hexane is used as the solvent for the fixing operation.

17. A process as claimed in any of claims 10, 11, 14 or 15, wherein the polymeric solid or the support-fixed complex rhodium compounds are aftertreated in one of more stages with hydrogen/carbon monoxide mixtures and/or with reducing agents, such as formaldehyde, alkali or alkaline-earth borohydride, hydrazine or aluminium alkyl, under total pressure of from about 10 to 300 bars and at temperature of from 50 to 200°C, preferably in the presence of a solvent such as benzene, toluene, xylene, *n*-hexane, cyclohexane, methyl cyclohexane, monoglyme, diethyl ether, tetrahydrofuran, dioxane and, in particular, lower alcohols.

18. The use of the monomeric, polymeric and support-fixed complex rhodium compounds claimed in the preceding Claims as catalysts for chemical reactions.

19. Complex of rhodium substantially as described with reference to any of the examples.